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# Investigation of the effect of preliminary modification of solutions on the properties of precipitated hydrated zirconium oxides

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**Abstract.** In this study, hydrated zirconium oxides and yttrium stabilized zirconia powders were synthesized by precipitation. Influence of preliminary solution modification, namely preliminary heating of the solutions and the addition of sulfate ions was investigated. It is shown that the addition of sulfate ions leads to a decrease in the size of aggregates and an increase in the specific surface area of the particles. The greatest increase in the specific surface area was observed during precipitation of a preliminary heated solution with the addition of sulfate ions.

## 1. Introduction

Zirconia ( $\text{ZrO}_2$ ) is a widely used ceramic material exhibiting excellent properties such as low thermal conductivity, high thermal stability, high oxygen ion conductivity, high strength, high fracture toughness and high thermal shock resistance enabling it to be used as thermal barrier coating, cutting tools, refractory material, as catalyst/catalyst support (stable under a reducing atmosphere and photo irradiation) [1]. Yttria stabilized zirconia (YSZ) is the most widespread electrolyte material for solid oxide fuel cell (SOFC) due to its high ionic conductivity and electronic resistivity over a wide range of oxygen partial pressures. In addition, it is chemically stable at high temperatures in oxidizing and reducing atmospheres, chemically and mechanically compatible with the other cell components and is gas tight [2].

To form SOFC electrolytes, finely dispersed YSZ powders with a high specific surface, low porosity, narrow particle size distribution and a high density are required. Many articles [3, 4] and patents [5, 6] discuss the addition of sulfate ions to produce zirconium oxide with desired properties or to produce sulfated zirconium [7]. Therefore, it is perspective to study the effects of the addition of sulfate ions, as well as the preliminary modification of the initial solution, namely preliminary heating of the solution, on the properties of YSZ powders obtained by precipitation of hydroxides.

## 2. Experimental

### 2.1. Preparation of samples

Zirconium nitrate and yttrium nitrate were used to prepare samples of zirconium oxide stabilized with 7% yttrium oxide. The salts were dissolved in distilled water in a pre-determined ratio.



Before starting the precipitation, 200 ml of distilled water was poured into the reactor. The first precipitation was carried out in a reactor with continuous stirring, aqueous ammonia solution was added to the acidic solution of zirconium and yttrium nitrates up to pH=5 (Sample 7YZr). (Sample 7YZr). The resulting suspension was filtered, dried at 120 °C (marked 120) for 24 hours and calcined at 800°C (marked 800) for 2 hours.

To prepare the second sample, sulfuric acid was added to the nitrate solution in the molar ratio of  $Zr/SO_4=1/0.5$  (Sample 7YZr-SO4). This solution was used to prepare the hydroxides as described previously.

To prepare the third sample, the nitrate solution was by heating it to 90 °C on a hot oil bath with constant stirring and cooled after that (Sample 7YZr-Pol). The obtained solution was used to prepare the hydroxides as described previously.

To obtain the fourth sample, the nitrate solution was heated to 90 °C on a hot oil bath with constant stirring and cooled after that. Then sulfuric acid was added to the nitrate solution in the molar ratio of  $Zr/SO_4=1/0.5$ , after that a white precipitate appeared which indicated the formation of the sol. Precipitation was performed as described above from this sol (Sample 7YZr-SO4-Pol).

## 2.2. Characterization

X-ray diffraction patterns of the samples were obtained on an XPertPro MPD diffractometer with a solid-state pixel detector in  $Cu_{K\alpha}$  radiation using a p-filter on a secondary beam. The Rietveld method of full-profile analysis using the XPert High Score Plus software was used. The size of the coherent scattering region was determined by the Sherrer method in reflections at small scattering angles (factor of the form  $K = 0.9$ ).

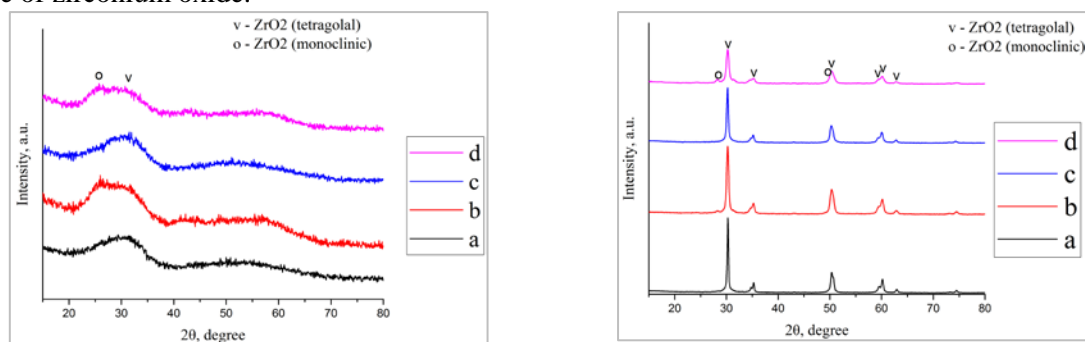
The particle size distribution was measured on an ANALYSETTE 22 NanoTec plus device (FRITSCH). The measurements were carried out in a water medium using a direct transmission scheme with an infrared and green laser (particle size measuring range from 0.08 to 2000  $\mu m$ ).

The study of specific surface area parameters and porosity of the samples was carried out on a Quantachrome NOVA 1200E device using the method of low-temperature nitrogen adsorption. Before measurement, the oxide samples were degassed under vacuum at a temperature of 290 °C for 1 hour, the dried samples were degassed under vacuum at a temperature of 120 °C for 2 hour.

SEM images were obtained using an electronic scanning microscope Carl Zeiss SIGMA VP in high-vacuum mode using an InLens detector. The accelerating voltage was 2 kV.

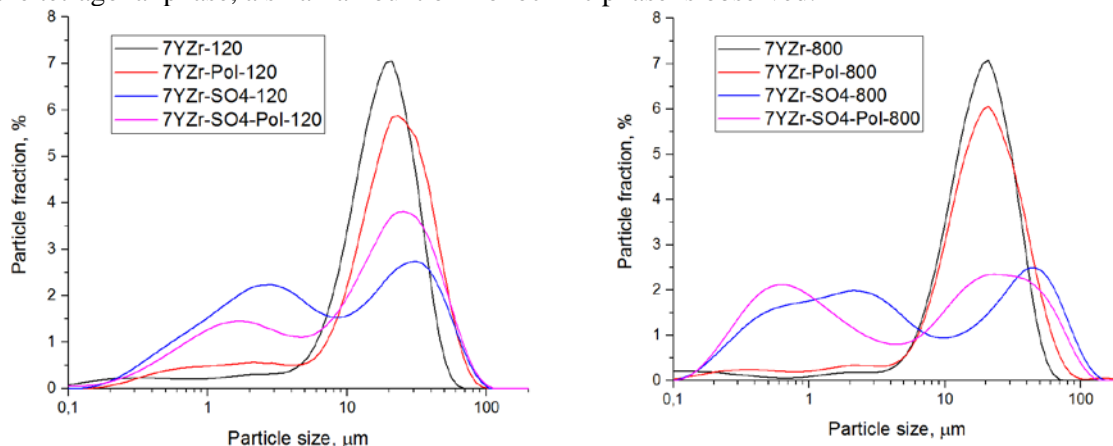
## 3. Result and discussion

Diffraction patterns of the samples after drying at 120 °C are shown in Fig. 1. All samples are amorphous; no phases were found in the samples. According to the location of the peaks, it can be assumed that samples 7YZr-120, 7YZr-SO4-120 are prone to formation of a tetragonal phase of zirconium oxide. Samples 7YZr-SO4-Pol-120, 7YZr-Pol-120 are prone to formation of a monoclinic phase of zirconium oxide.



**Figure 1.** X-ray diffraction patterns of samples after drying at 120 °C (1): (a) – 7YZr-120, (b) – 7YZr-Pol-120, (c) – 7YZr-SO4-120, (d) – 7YZr-SO4-Pol-120; and after calcination at 800 °C (2): (a) – 7YZr-800, (b) – 7YZr-Pol-800, (c) – 7YZr-SO4-800, (d) – 7YZr-SO4-Pol-800.

Diffraction patterns of the samples after calcination at 800 °C are shown in figure 2. Only sample 7YZr-SO4-800 has a completely tetragonal zirconium oxide phase; in the remaining samples, in addition to the tetragonal phase, a small amount of monoclinic phase is observed.



**Figure 2.** The differential distribution of ZrO<sub>2</sub> particles by size after (a) - drying at 120 °C, (b) - calcination at 800 °C.

Table 1 shows the size of coherent scattering region and the fraction of the monoclinic phase in the samples after calcination at 800 °C. The largest crystallite size of the tetragonal phase is observed in sample 7YZr-800. Preliminary heating of the solution, as well as the addition of sulfate ions, leads to a decrease in the crystallite sizes of the tetragonal phase of zirconium oxide, this may be due to a change in polymer bonds in the initial nitrate solution, and, consequently, a change in the nucleation of particles during precipitation. Preliminary heating of the solution greatly reduces the crystallite size of the tetragonal phase of zirconium oxide than the addition of sulfate ions. The largest amount of the monoclinic phase (16.5%) is observed in sample 7YZr-SO4-Pol-800, this sample also has the smallest crystallite size of the tetragonal phase.

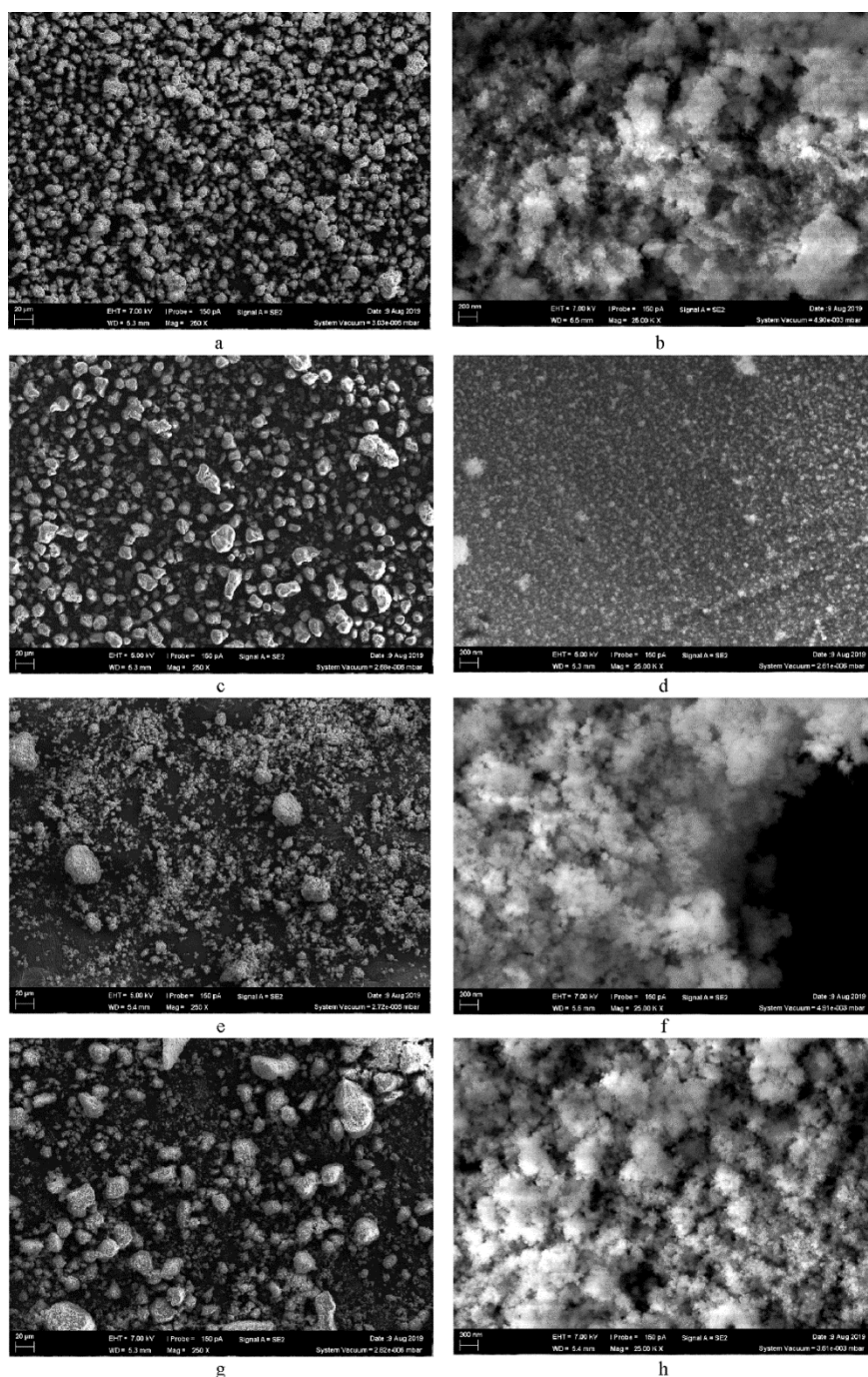
**Table 1.** Coherent scattering region of samples after calcination at 800°C.

	ZrO <sub>2</sub> -Tetragonal (A)	ZrO <sub>2</sub> -Monoclinic (A)	Monoclinic (%)
7YZr-800	308	29	5.2
7YZr-Pol-800	178	69	7.5
7YZr-SO4-800	208	-	-
7YZr-SO4-Pol-800	136	93	16.5

Differential distribution of ZrO<sub>2</sub> particles by size is shown in figure 2. After drying at 120 °C, the main peak of the samples is at 20 μm. Samples synthesized without sulfate ions have a monomodal particle size distribution close to Gaussian. Samples synthesized with the addition of sulfate ions exhibit a bimodal particle size distribution, the first peak at about 2 μm, the second at 20 μm. After calcination at 800 °C, the samples synthesized without sulfate ions retain a particle size distribution close to normal with a peak at 20 μm. In samples 7YZr-SO4-800 and 7YZr-SO4-Pol-800, a decrease in the fraction of particles of about 20 μm is observed, in sample 7YZr-SO4-Pol-800, a shift of the fine fraction peak from 2 μm to 0.6 μm is observed. It can be assumed that sulfate ions interact with zirconium with the formation of hydroxosulphates (which are embedded in the structure) and during thermal processing, sulfate decomposition occurs which results in the destruction of aggregates.

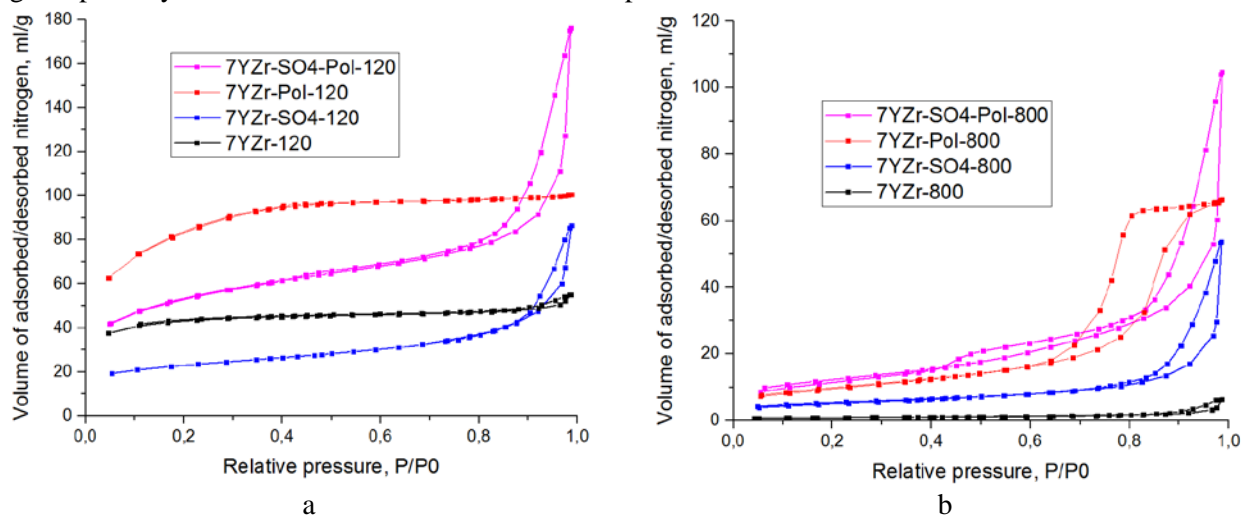
The SEM images of samples after drying at 120 °C are shown in figure 3. The particle sizes of all samples are consistent with the laser diffraction data. Aggregates of sample 7YZr-120 have a nearly globular shape, their size is approximately the same - 15-20 microns, these globes are porous, composed of small amorphous primary particles. Sample 7YZr-Pol-120 particles have a nearly globular shape. These particles have the most round shape, smoothest borders, and are composed of almost globular

particles, they also have a fairly narrow particle size distribution of 15-20 microns, which is consistent with the particle size distribution. This sample also has the densest aggregates in comparison with other samples and consists of the largest primary particles of about 20 nm. Sample 7YZr-SO<sub>4</sub>-120 has large globular aggregates of about 20  $\mu\text{m}$ , as well as a small fraction (less than 1  $\mu\text{m}$ ). These aggregates consist of primary particles and are less porous than that of sample 7YZr. Finally, sample 7YZr-SO<sub>4</sub>-Pol-120 aggregates have an irregular shape, and their sizes are different. Large aggregates (about 30  $\mu\text{m}$ ) and very small (less than 1  $\mu\text{m}$ ) are present, and consist of primary particles, the porosity of the sample is similar to sample 7YZr-120.



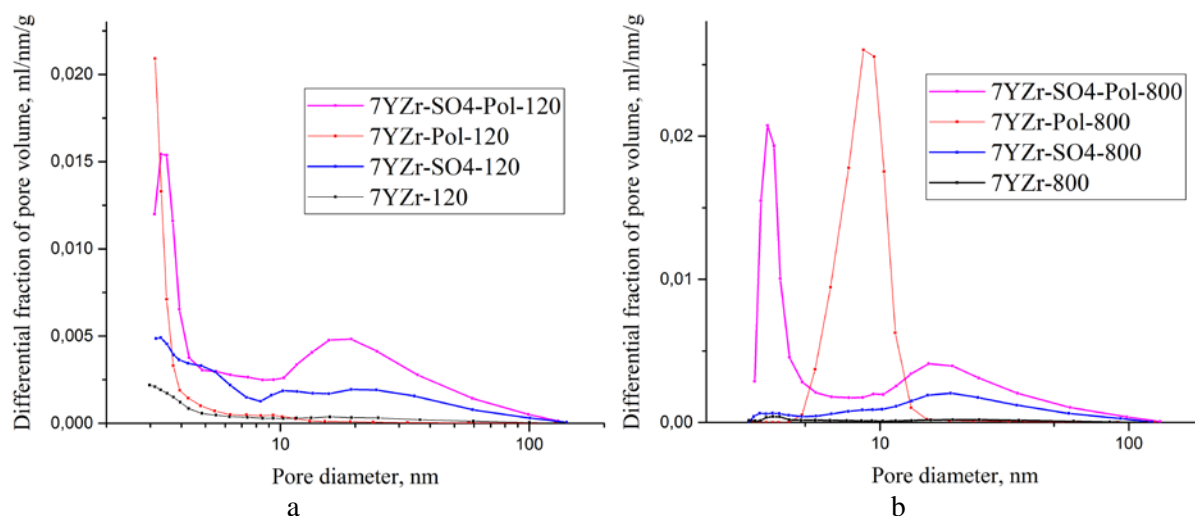
**Figure 3.** SEM photos of particles after drying obtained from solutions: (a, b) – 7YZr-120; (c, d) – 7YZr-Pol-120; (e, f) – 7YZr-SO<sub>4</sub>-120; (g, h) – 7YZr-SO<sub>4</sub>-Pol-120.

Figure 4 shows nitrogen adsorption and desorption isotherms of samples dried at 120 °C and calcined at 800 °C. Types of isotherms can be determined by utilizing the IUPAC classification. Samples 7YZr-120, 7YZr-800 and 7YZr-Pol-120 are characterized by type I, the remaining samples by type IV. Pore shapes can be determined by the shape of the hysteresis loops on the isotherms. According to the classification of hysteresis forms, 3 types of pore shapes are distinguished: cylindrical, slit-like and bottle-shaped [8]. For samples 7YZr-120, 7YZr-800 and 7YZr-Pol-120, micropores with a slit-like shape less than 3 nm are typical, pores of a bottle-shaped form are observed for sample 7YZr-Pol-800, for the other samples slit-like micropores and slit-like pores formed by flat particles are typical. The highest porosity is observed in the 7YZr-SO<sub>4</sub>-Pol sample.



**Figure 4.** Nitrogen adsorption and desorption isotherms of samples after (a) - drying at 120 °C, (b) - calcination at 800 °C.

Figure 5 shows pore size distributions. Samples dried at 120 °C have pores of about 3 nm; samples 7YZr-SO<sub>4</sub>-120 and 7YZr-SO<sub>4</sub>-Pol-120 also have mesopores in the range from 10 to 100 nm. After calcination at 800 °C, sample 7YZr-800 has only micropores smaller than 3 nm, samples 7YZr-SO<sub>4</sub>-800 and 7YZr-SO<sub>4</sub>-Pol-800 have a bimodal pore size distribution with peaks at about 3 nm and about 18 nm, sample 7YZr-Pol-800 has a pore size distribution close to normal with a peak at 10 nm.



**Figure 5.** Pore size distribution of samples after (a) - drying at 120 °C, (b) - calcination at 800 °C.



Table 2 shows the specific surface and porosity parameters of samples. It is shown that of the dried samples, samples 7YZr-SO4-Pol and 7YZr-Pol have the largest specific surface area of 171 and 268 m<sup>2</sup>/g, respectively. After calcination, these samples also have the highest specific surface area, but it decreased to 34 and 41 m<sup>2</sup>/g, respectively. It can be concluded that precipitation from a preliminary heated solution significantly increases the specific surface area and it remains quite high even after calcination. After drying, the 7YZr-120 sample has a rather high surface, but after calcination it sharply decreases to the lowest value of 2.5 m<sup>2</sup>/g. It can be noted that for samples in which the mesopores make a greater contribution to the specific surface, the surface remains quite high after calcination, while for samples in which micropores make a greater contribution to the specific surface, the specific surface of the samples decreases sharply. It can be concluded that the developed microporosity collapses during calcination. After calcination, the samples show an increase in the average pore diameter.

**Table 2. Specific surface area and porosity parameters.**

Sample	Specific Surface Area (m <sup>2</sup> /g)	Specific Micropore Surface (m <sup>2</sup> /g)	Specific Mesopore Surface (m <sup>2</sup> /g)	Pore Volume (ml/g)	Average Pore Diameter (nm)
7YZr-120	125.2	82.4	42.8	0.0850	2.7
7YZr-Pol-120	267.7	72.6	195.1	0.1556	2.3
7YZr-SO4-120	72.6	27.9	44.7	0.1336	7.4
7YZr-SO4-Pol-120	170.9	51.3	119.7	0.2725	6.4
7YZr-800	2.4	0.2	2.2	0.0010	16.3
7YZr-Pol-800	34.0	1.4	32.6	0.1025	12.1
7YZr-SO4-800	17.4	3.7	13.7	0.0832	19.1
7YZr-SO4-Pol-800	41.0	3.5	37.5	0.1620	15.8

#### 4. Conclusion

Modification of the initial solutions of zirconium and yttrium nitrates significantly affected the properties of hydrated zirconium and yttrium stabilized zirconium oxide before and after calcination at 800 °C. Preliminary heating of the initial solution and the addition of sulfate ions led to a decrease in the size of the coherent scattering region. Heating the initial solution led to an increase in the specific surface area of the samples after drying at 120 °C and the high values of the specific surface after calcination at 800 °C. It was shown that the addition of sulfate ions reduces the size of the aggregates, and after calcination, they crumble into smaller ones, and in a sample with only sulfate ions, the large fraction peak increases significantly. Also, the addition of sulfate ions promotes the formation of a loose structure in the samples. Dense globular zirconium oxide powders can be used to create nonporous ceramic coatings. Samples with high porosity and specific surface can be used to form ceramic products by the slip casting method.

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